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Photoelectron Spectroscopy of  $\text{Si}_2^-$

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T. N. Kitsopoulos and D. M. Neumark

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Department of Chemistry  
University of California  
Berkeley, CA 94720

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# PHOTOELECTRON SPECTROSCOPY OF $\text{Si}_2^-$

THEOFANIS N. KITSOPOULOS AND DANIEL M. NEUMARK

Department of Chemistry

University of California at Berkeley

Berkeley CA 94720

## ABSTRACT

In this report we discuss the photoelectron spectrum of  $\text{Si}_2^-$  obtained at 355 nm. The spectrum shows a series of transitions to the low-lying triplet states of  $\text{Si}_2$  as well as transitions to the higher-lying singlet states. Several possible assignments of the anion and neutral triplet states are presented.

## INTRODUCTION

In recent years understanding chemical bonding in clusters has been the focus of intense research[1]. Monitoring the evolution of the properties of clusters as a function of size is of primary interest since this will lead to a better understanding of cluster chemistry. The determination of vibrational frequencies and the energetics of low-lying electronic states represents an important step towards the characterization of clusters[2],[3],[4].

In the past six months we have been studying silicon clusters using negative ion photoelectron spectroscopy[5], [6], [7], [8]. Using this method we were able to obtain the vibrationally resolved spectra of  $\text{Si}_2^-$ ,  $\text{Si}_3^-$  and  $\text{Si}_4^-$ . A detailed discussion of our photoelectron spectra for  $\text{Si}_3^-$  and  $\text{Si}_4^-$  has been presented elsewhere[9]. This report will be concerned only with the spectroscopy of  $\text{Si}_2$  and  $\text{Si}_2^-$ .

Unlike  $\text{C}_2$  and  $\text{C}_2^-$ , which have been characterized thoroughly[10],[11], the spectroscopic information on  $\text{Si}_2$  is limited, while  $\text{Si}_2^-$  has never been spectroscopically identified. Using emission spectroscopy, Douglas[12] identified both the  $^3\Sigma_g^-$  ground state and the  $^3\Pi_u$  first excited state for the neutral dimer. However, direct emission or absorption between these two states has not been observed and thus the  $^3\Sigma_g^-$ - $^3\Pi_u$  splitting remains undetermined. Several ab initio calculations predict these two states to be very close in energy, with splittings ranging from 20 to 50 meV[13],[14],[15],[16]. The first two electronic states for the anion ( $^2\Pi_u$  and  $^2\Sigma_g^+$ ) are also predicted to be nearly degenerate[17],[18]. In 1987, by obtaining the photoelectron spectrum of  $\text{Si}_2^-$ , Nimlos et.al. assigned the  $^3\Sigma_g^-$ - $^3\Pi_u$  and the  $^2\Sigma_g^+$ - $^2\Pi_u$  splittings to be  $0.053 \pm .015$  eV and  $0.117 \pm .016$  eV respectively[19].

Our spectra of  $\text{Si}_2^-$ , obtained at higher resolution than the previous photoelectron work, reveal additional structure which was previously unresolved and lead us to question the assignment of Nimlos. In addition, we observe transitions to higher electronic states of  $\text{Si}_2$  than were seen previously.

## Experimental

The experimental apparatus used in this work is a modified version of our time-of-flight photoelectron spectrometer described in detail elsewhere[20]. A beam of silicon cluster anions is mass selected by time of flight and the cluster of interest is photodetached with a pulsed laser. A small fraction ( $10^{-4}$ ) of the ejected photoelectrons are energy analyzed by time of flight. The electron energy resolution is 8 meV ( $64 \text{ cm}^{-1}$ ) for electrons with .65 eV kinetic energy, and degrades as  $(\text{KE})^{3/2}$ . The spectra here were obtained with the third harmonic of a Nd:YAG laser at 355 nm, at 20 Hz repetition rate and each spectrum was signal averaged for 80,000 laser shots. Spectra were obtained at two laser polarization angles,  $\theta = 0^\circ$  and  $90^\circ$ , with respect to the

direction of electron detection. The polarization dependence of the photoelectron intensity distribution is crucial in our analysis.

The silicon negative ion clusters were generated with a laser vaporization/pulsed molecular beam source[21]. The output of a XeCl excimer laser (308 nm, 5-15 mJ/pulse) was focused onto the surface of a rotating and translating silicon rod. The resulting plasma vapor was entrained in a pulse of He from a pulsed solenoid valve (0.05 cm diameter orifice), and expanded through a 0.25 cm diameter, 1.25 cm long channel into the vacuum chamber. Varying the length of this expansion channel shifts the mass range of the cluster distribution. This particular length was found to optimize production of  $\text{Si}_3^-$  and  $\text{Si}_4^-$ . To produce enough  $\text{Si}_2^-$  for our experiment, it was necessary to operate the source at very low He backing pressures. This most likely results in vibrationally hot dimer anions, many of which are probably produced by fragmentation of higher clusters. The vibrational temperature for the photoelectron spectrum of  $\text{C}_2^-$  obtained using in the same source was found to be near 3000 K, and we estimate this to be the  $\text{Si}_2^-$  vibrational temperature as well.

## Results

Our photoelectron spectra of  $\text{Si}_2^-$  obtained at 355 nm ( $h\nu = 3.49$  eV) and  $\theta = 0^\circ$  and  $90^\circ$  are presented in Figures 1 and 2. The electron kinetic energy (eKE) is related to the internal (vibrational + electronic) energy of the anion  $E^{(-)}$  and neutral  $E^{(0)}$  by

$$eKE = h\nu - EA - E^{(0)} + E^{(-)}, \quad (1)$$

where EA is the electron affinity of the neutral ground state. Two groups of transitions are observed. Peaks A-F are in the same energy range as the peaks seen by Nimlos and correspond to transitions to the triplet states of  $\text{Si}_2$ , while peaks G-L are most likely due to transitions to the higher-lying singlet states. Photodetachment at higher photon energy, 266 nm (4.66 eV), revealed no new features.

Figure 1: Shown is the photoelectron spectrum of  $\text{Si}_2^-$  obtained at 355 nm (3.49 eV), with the laser polarization parallel to the direction of electron detection.

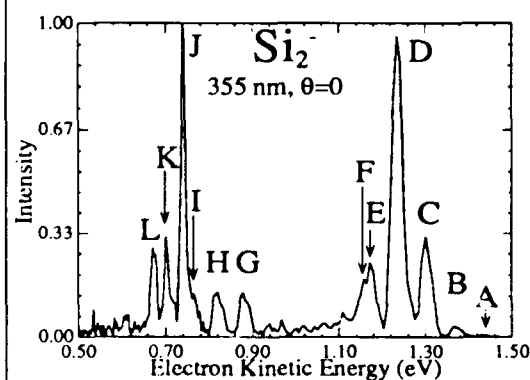
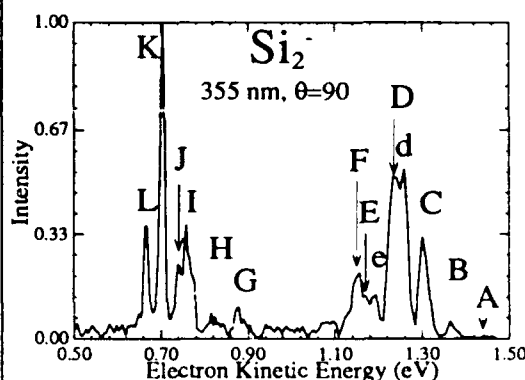


Figure 2: Shown is the photoelectron spectrum of  $\text{Si}_2^-$  obtained at 355 nm (3.49 eV), with the laser polarization perpendicular to the direction of electron detection.



Figures 1 and 2 show that varying the laser polarization changes the peak intensities in different ways. Peaks D and E are considerably more intense at  $\theta = 0^\circ$  than at  $\theta = 90^\circ$ . Peaks B, C, and F are relatively insensitive to laser polarization. Peaks d and e are not evident in the  $\theta = 0^\circ$  spectrum. As discussed below, the presence of three sets of peaks with different polarization dependences suggests the presence of three anion  $\rightarrow$  neutral electronic transitions. The singlet band also shows three sets of peaks. Peaks G, H and J have maximum intensity at

A-1

$\theta=0^\circ$ , peaks I and K are most intense at  $\theta=90^\circ$ , and peak L has the same intensity at both laser polarizations.

The spectra in Figures 1 and 2 differ from those previously obtained by Nimlos[19]. They used a lower photon energy (2.54 eV) and only observed four peaks (A-D). In addition, they did not resolve the D,d doublet in Figure 1.

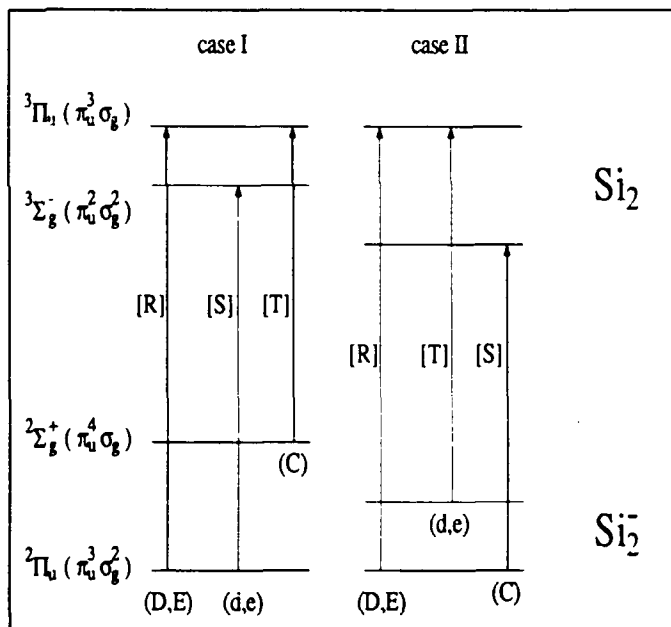
## Discussion

We are primarily concerned with the triplet band, peaks Through F. We interpret our spectra with the aid of previous ab initio results for the anion and neutral as well as experimental results for the neutral. Recent ab initio calculations by Raghavachari and Rohlfing[18] predict for the first two states of  $\text{Si}_2^-$  predict bond lengths and stretching frequencies found of 2.124 Å and 579  $\text{cm}^{-1}$  for the  $^2\Sigma_g^+$  state and 2.202 Å and 539  $\text{cm}^{-1}$  for the  $^2\Pi_u$  state. However as was the case in an earlier calculation by Bruna[17], the splitting and even the ordering of these states is uncertain.

For  $\text{Si}_2$  the spectroscopic constants have been determined experimentally[12],[11] and are 2.246 Å, 511  $\text{cm}^{-1}$  for  $^3\Sigma_g^-$  ground state, and 2.155 Å, 548  $\text{cm}^{-1}$  for the  $^3\Pi_u$ . Calculations by Bauschlicher[16] estimate the  $^3\Sigma_g^-$ - $^3\Pi_u$  gap to be  $440 \pm 100 \text{ cm}^{-1}$  ( $55 \pm 12 \text{ meV}$ ) while calculations by Bruna et.al.[13] predict a much smaller splitting of 20 meV. However, the consensus among theoreticians is that the  $^3\Sigma_g^-$  state is the ground state.

Drawn below are the transitions between the two lowest levels of the anion and the neutral silicon dimer.

We have assumed that the  $^2\Pi_u$  is the ground state of  $\text{Si}_2^-$  and we will present an alternative situation later. In a typical photoelectron spectrum, one only observes transitions between anion and neutral electronic states which involve the removal of a single electron (one-electron transitions) By this rule, three of the four possible electronic transitions among these four states are allowed; only the  $^2\Sigma_g^+ \rightarrow ^3\Sigma_g^-$  transition is not allowed. The three allowed electronic transitions are the  $^2\Pi_u \rightarrow ^3\Pi_u$ ,  $^2\Pi_u \rightarrow ^3\Sigma_g^-$  and the  $^2\Sigma_g^+ \rightarrow ^3\Pi_u$  which we will call [R], [S] and [T] respectively, maintaining the same notation used by Nimlos et.al.[19]. Nimlos assigned peaks B, C, and D to transitions [T], [S], and [R], respectively. The additional peaks in our spectrum lead us to a different assignment.



The major hurdle in assigning the  $\text{Si}_2^-$  spectrum comes about because the vibrational frequencies in the anion and neutral are all about the same and are comparable to the predicted splittings between the low-lying electronic states in the anion and neutral. The polarization results are very useful in this regard, as peaks whose intensities show similar dependence on polarization can be assigned to the same anion  $\rightarrow$  neutral electronic transition. On this basis (see Results), we assign peaks D and E to a vibrational progression associated with one electronic transition, peaks d and e to a vibrational progression associated with another transition, and peaks B and C to a third electronic transition.

The next step is to assign the various sets of peaks to particular electronic transitions [R], [S], and [T]. As pointed out by Nimlos[19], [S] and [T] involve removal of a  $\pi_u$  electron from the  $\text{Si}_2^-$ , and this should lead to an isotropic (s-wave) photoelectron angular distribution near the

detachment threshold. On the other hand, [R] involves removal of a  $\sigma_g$  electron, yielding a highly anisotropic angular distribution near threshold. If only one set of peaks showed a strong polarization dependence, we would assign it to a p-wave transition and the other two to s-wave transitions. Unfortunately, two sets of peaks have anisotropic angular distributions. We have previously observed that transitions which go via s-wave detachment near threshold can exhibit anisotropic angular distributions at high electron kinetic energies ( $>0.5$  eV) due to contributions from higher partial waves. Thus, while peaks B and C, which do exhibit an isotropic angular distribution, can be assigned to [S] or [T] (i.e. s-wave detachment), the assignment of the other two sets of peaks is problematic.

Assuming that the  $\text{Si}_2^-$  ground state is the  $^2\Pi_u$  state, either of the two assignments drawn below is possible. In both, peaks D and E are assigned to the electronic transition [R]. In case I, peaks d and e are assigned to [S] and B and C are assigned to [T]. The energy intervals consistent with our spectra are 25 meV for the  $^3\Pi_u$ - $^3\Sigma_g^-$  splitting and 67 meV for the  $^2\Sigma_g^+$ - $^2\Pi_u$  splitting. Table I shows the detailed peak assignments consistent with case I.

Table I:

Peak	Position(eV)	$\text{Si}_2^- \rightarrow \text{Si}_2$ Transition
A	2.052	$^2\Sigma_g^+(v''=2) \rightarrow ^3\Pi_u(v'=0)$
B	2.129	$^2\Sigma_g^+(v''=1) \rightarrow ^3\Pi_u(v'=0)^*$ $^2\Pi_u(v''=2) \rightarrow ^3\Sigma_g^-(v'=0)$ $^2\Pi_u(v''=2) \rightarrow ^3\Pi_u(v'=0)$
C	2.192	$^2\Sigma_g^+(v''=0) \rightarrow ^3\Pi_u(v'=0)^*$ $^2\Pi_u(v''=1) \rightarrow ^3\Sigma_g^-(v'=0)$ $^2\Pi_u(v''=1) \rightarrow ^3\Pi_u(v'=0)$
d	2.234	$^2\Pi_u(v''=0) \rightarrow ^3\Sigma_g^-(v'=0)$
e	2.298	$^2\Pi_u(v''=0) \rightarrow ^3\Sigma_g^-(v'=1)$
D	2.259	$^2\Pi_u(v''=0) \rightarrow ^3\Pi_u(v'=0)$
E	2.323	$^2\Pi_u(v''=0) \rightarrow ^3\Pi_u(v'=1)$

If more than one transition contributes to a peak, the dominant transition is indicated with a (\*). Note that peaks D and E are a vibrational progression in the neutral  $^3\Pi_u$  state, d and e are a progression in the neutral  $^3\Sigma_g^-$  state, while A and B are 'hot' band transition from vibrationally excited anions.

We can learn about the anion and neutral bond lengths by simulating the peak intensities in a Franck-Condon analysis, using the experimental and ab initio bond lengths as a guide. Taking the  $^3\Sigma_g^-$  bond length ( $R_e$ ) to be 2.246 Å, the d/e intensity ratio yields  $R_e = 2.216 \pm 0.01$  Å for the anion  $^2\Pi_u$  state, which is close to the ab initio value of 2.202 Å. Assuming  $R_e = 2.216$  Å for the anion  $^2\Pi_u$  state, the D/E intensity ratio yields  $R_e = 2.185$  Å for the neutral  $^3\Pi_u$  state, which should be compared to the experimental value of 2.155 Å. If we assume  $R_e = 2.155$  Å for the neutral  $^3\Pi_u$  state and a vibrational temperature of 3000 K for the anions, the B/C ratio yields  $R_e = 2.130$  Å for the anion  $^2\Sigma_g^+$  state, which is close to the ab initio result of 2.124 Å. This analysis is quite crude and merely shows that case I cannot be excluded on the basis of the intensities in our spectrum.

Let us now consider case II where the  $^3\Pi_u$ - $^3\Sigma_g^-$  splitting is 67 meV and the  $^2\Sigma_g^+$ - $^2\Pi_u$  splitting is 25 meV. In this case, peaks d and e are assigned to [S] while B and C are assigned to [T]. Using the experimental bond lengths for the  $^3\Sigma_g^-$  and  $^3\Pi_u$  states, Franck-Condon simulations of our spectra similar to those describe above yield anion bond distances of 2.125 Å for the  $^2\Sigma_g^+$  state and 2.216 Å for the  $^2\Pi_u$  state. These geometries again agree well with the

ab initio results on  $\text{Si}_2^-$ . The detailed case II assignment is summarized in the table II below. Note that in contrast to case I, peaks d and e are assigned to a progression in the neutral  $^3\Pi_u$  state. The only reason to favor case II over case I at this point is that the neutral splitting in case II is closer to the Bauschlicher's ab initio value.

Table II:

Peak	Position (eV)	$\text{Si}_2^- \rightarrow \text{Si}_2$ Transition
A	2.052	$^2\Pi_u (v''=2) \rightarrow ^3\Sigma_g^+ (v'=0)$
B	2.129	$^2\Pi_u (v''=1) \rightarrow ^3\Sigma_g^+ (v'=0)^*$ $^2\Pi_u (v''=2) \rightarrow ^3\Pi_u (v'=0)$ $^2\Sigma_g^+ (v''=2) \rightarrow ^3\Pi_u (v'=0)$
C	2.192	$^2\Pi_u (v''=0) \rightarrow ^3\Sigma_g^+ (v'=0)^*$ $^2\Pi_u (v''=1) \rightarrow ^3\Pi_u (v'=0)$ $^2\Sigma_g^+ (v''=1) \rightarrow ^3\Pi_u (v'=0)$
d	2.234	$^2\Sigma_g^+ (v''=0) \rightarrow ^3\Pi_u (v'=0)$
e	2.298	$^2\Sigma_g^+ (v''=0) \rightarrow ^3\Pi_u (v'=1)$
D	2.259	$^2\Pi_u (v''=0) \rightarrow ^3\Pi_u (v'=0)$
E	2.323	$^2\Pi_u (v''=0) \rightarrow ^3\Pi_u (v'=1)$

A third possible assignment arises when we allow the  $^2\Sigma_g^+$  state rather than the  $^2\Pi_u$  state to be the ground electronic state of  $\text{Si}_2^-$ . An assignment consistent with our spectra has the  $^3\Pi_u$ - $^3\Sigma_g^+$ -splitting at 42 meV and the  $^2\Pi_u$ - $^2\Sigma_g^+$  splitting at 25 meV. In this case, peaks B and C are assigned to [S], peaks d and e to [R], and peaks D and E to [T]. As in case II, peaks d,e and D,E are vibrational progressions in the neutral  $^3\Pi_u$  state. As mentioned above, the identity of the anion ground state is not clear from the ab initio results, so this third possibility cannot be excluded.

We have presented three alternative assignments for the photoelectron spectrum of  $\text{Si}_2^-$ . Further justification can only come from obtaining better quality spectra. We are trying to accomplish this using our threshold photodetachment spectrometer[22]. One advantage of this instrument is its improved cluster source, capable of producing cold ions. Photodetachment of cold anions would eliminate or at least identify all the hot band transitions in our spectra, which are transitions originating from excited anion states. Another advantage is the considerably higher resolution of this instrument,  $3 \text{ cm}^{-1}$ , which would allow us to resolve transitions like the ones predicted to lie under peaks C and B. In addition, the higher resolution will allow us to unambiguously identify vibrational progressions in the neutral with either the  $^3\Sigma_g^+$  state or the  $^3\Pi_u$  state. Finally, the threshold spectrometer is only sensitive to anion $\rightarrow$ neutral transitions that proceed via s-wave detachment. This will eliminate several of the peaks seen in the photoelectron spectrum thereby simplifying the identification of peaks with electronic transitions.

## Conclusion

Our photoelectron spectra of  $\text{Si}_2^-$  have shown that the correct identification of the low lying states in silicon dimer are far from complete. Our spectra reveal several additional electronic states which lie within 1 eV of the ground state. Since the positions of these states have now been identified we are hoping that our results will stimulate high resolution IR experiments that will completely characterize this elusive diatomic molecule.

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